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Citation for published version:
Rojas Alva, U, Fritt-Rasmussen, J & Jomaas, G 2020, 'Small-scale in-situ burning (ISB) experiments with chemically confined crude oils on water', *Fire Safety Journal*. https://doi.org/10.1016/j.firesaf.2020.103135

Digital Object Identifier (DOI):
10.1016/j.firesaf.2020.103135

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Peer reviewed version

Published In:
Fire Safety Journal

Small-scale in-situ burning (ISB) experiments with chemically confined crude oils on water

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Abstract

Small-scale experiments were performed in a custom-made laboratory rig to study the in-situ burning (ISB) behaviour for oils that were chemically confined using herders. The burning efficiency, the global mass burning rate and the regression rate are all reported. Two commercially available herding agents (ThickSlick 6535 and OP40) were used to thicken two crude oils (Alaska North Slope (ANS) and Grane), and their respective artificial water-in-oil emulsions. The burning behaviour during ISB was found to be affected by the oil type and weathering degree. However, no dependencies were observed on the burning behaviour regardless of the herder type. The chemical confinement resulted in quantitative lower burning results (burning efficiency, mass burning rate and regression rate) as compared to physical confinement. Scaling dependencies were also found as a function of the oil amount or oil diameter with contrasting qualitative dependencies between the results from experiments with respectively chemical and physical confinement.

Nomenclature

A_s	Oil slick area $[cm^2]$	$\dot{r}''$	Regression rate $[mm/min]$
BE	Burning efficiency [%]	ρ_0	Initial oil density $[g/cm^3]$
D	Pool diameter [m]	ρ_f	Final oil density $[g/cm^3]$
ΔH_c	Heat of combustion $[KJ/g]$	t_b	Burning time [s]
m_0	Initial oil mass [g]	τ_{oil}	Initial oil slick thickness [mm]
m_f	Final oil mass [g]		
$\dot{m}_{global}$	Global mass burning rate $[g/s]$		

Keywords: In-situ burning, herding, burning behaviour, burning efficiency, regression rate

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1. Introduction

To remediate an oil spill in the sea, the three main cleaning methods are mechanical recovery, chemical dispersing and in-situ burning. Physical countermeasures include, in general terms, confinement of the oil by containment booms followed by skimming and pumping of the oil into storage tanks. The use of chemical dispersants increases the natural dispersion of the oil. Burning of the oil spill on site, in-situ burning (ISB), where the oil is physically contained (within fire booms), and ignited in order to achieve self-sustained burning.

ISB can be defined as a controlled burning/combustion of an oil spill where the hydrocarbon components are mostly converted into carbon dioxide, water (vapor), soot and other components, which are released to the atmosphere [1], and a residue is left on the water surface. From the mid-70s, experimental research has been conducted on ISB, and it has been shown that the method is highly effective, as it can reach burning efficiencies above 80% in the best cases [1,2]. Thus, the method is well recognized to be an efficient way to remove oil and has been used in real oil spill incidents, latest in the Deepwater Horizon oil spill in the Gulf of Mexico [3].

A successful application of ISB of oils on open waters depends on many factors, one of which is a minimum oil slick thickness [1,4]. The thickness of the oil slick plays an important role to achieve successful ignition and subsequently a sustained burn of the oil. During the ignition process, the crude oil is heated (externally), thus producing vapor that mix with the oxidizer (in the air), eventually resulting in a flammable mixture. Flame spread will occur if the energy losses are lower than the heat generated during combustion. Therefore, a certain oil slick thickness is needed to reduce the heat losses towards the underlying, cold water bed. Under open sea conditions, the oil spill will spread, aided by sea and weather conditions, leading to a slick thickness less than 0.001 mm (sheens). Hence, fire booms are necessary to confine the oil spill in order to obtain the minimum oil slick thickness. Minimum ignitable thickness values, depending on the oil-weathering state, are empirically determined and established as a rule of thumb in literature for practical purposes [1]. The minimum ignitable thicknesses for fresh crude and emulsified crude oils are 1 mm and 2-3 mm, respectively. The use of fire booms can be challenging in ice-infested waters and remote locations in the Arctic. The time needed to deploy the fire booms can easily surpass the window-of-opportunity of burning the crude oil, and fire booms are not operative when there is a large amount of ice [5]. Thus, to thicken the oil slick, the use of herding agents (also named chemical surfactants/herders) might be an alternative to mechanical confinement with fire booms.

Herding agents are spread onto the water surface next to the spilled oil, where it rapidly forms a monomolecular layer, which owing to its high spreading pressure reduces the surface tension of the surrounding water from 70 mN/m to 20-30 mN/m [6]. When the herder monolayer reaches the oil slick edges (oil have spreading pressures in the range 10 to 20 mN/m) the oil contracts and much thicker oil layers are achieved owing to the equilibrium of interfacial forces [1,6]. Since the 1970s, the ability of herding agents as chemical confinement for an oil spill has been experimentally demonstrated, and various chemical surfactants have been employed [1,2]. Using the herding agents in connection with the ISB method has also been subject to experimental investigations in water tanks of various sizes [1,6–9]. These studies demonstrated the viability of herding agents for successful ISB even in ice-infested waters [6]. The few experiments carried out in the field also showed promising results (large burning efficiencies) [10].

Another factor, besides the oil slick thickness, that can play a significant role in the success of the ISB method is the weathering of the oil changing the behaviour and properties of the oil once spilled on the water [1,11–13]. The specific weather conditions and the properties of the oil will influence the weathering. Two of the most significant weathering processes are evaporation and emulsification. During evaporation, the volatile and semi-volatile compounds evaporate, and the evaporation rate will depend on the content of these light hydrocarbon compounds in the spilled crude oil [14]. The consequence of the evaporation process leads to an increase of the oil's physical and chemical properties such as density, flash point, pour point, viscosity and relative content of waxes and asphaltenes [14,15].

In the case of water-in-oil emulsification, the spilled crude oil mixes with seawater droplets depending on the content of surfactant-like components in the crude oil and due to weather conditions (wind speed and wave movements). Asphaltenes and resins are the heaviest (molecular weight) and most polar compounds in crude oils [16]. Asphaltenes, together with resins will behave as surfactant-like compounds to form emulsions, and both will also affect the stability of the emulsions [17]. The polarity of these components can vary, especially of asphaltenes, but only the most polar and most condensed resins and asphaltenes are the most effective emulsion stabilisers [16]. Hence, the content of these components in the composition of crude oil will determine the emulsion formation. The onset and stabilisation of emulsion on open waters occur when the density and viscosity of the crude oil increase (due to evaporation of the non-polar saturates and waxes compounds) and when the sea energy suffices to mix water and the oil [18] and they will support the emulsification process. As a consequence, the spilled oil increases in volume and viscosity, substantially affecting recovery [14].

The evaporation of the light compounds influences the ignition and subsequent flame spread, but it has a small effect on the overall burning behaviour on the in-situ burning [1,19,20]. By contrast, the emulsification process and the degree of water content in the artificial water-in-oil emulsions have a large impact on the ignitability and burnability [1,21]. The reduction in both burning processes can be explained by the heat and mass transfer mechanism during ignition and flame spread as compared to the burning of fresh crude oil. More energy would be required to raise the weathered oil to its flash point (increased owing to evaporation), and additional energy is also needed to break the emulsion into an oil layer placed above the weathered oil layer. As the water content increases in the emulsion over time, the weathered crude oil is no longer ignitable (by practical means) at a certain point, and this defines the window-of-opportunity of the ISB method [22].

For an oil spill in Arctic waters, the time frame to reach the oil before it passes its window-of-opportunity for ISB is crucial. Therefore, herding agents can be a faster solution to confine the oil spill. Most of the experimental ISB studies with herding agents conducted so far have focused on fresh crude oils [6,8,10], being the exception the study reported by Buist et al. [23]. In a real case scenario in the Arctic, operators might find the spilled oil already weathered when implementing the ISB method. Thus, it is important to expand the knowledge base also to include studies on the ability of the herding agents to contract emulsions. In addition, previous experimental work has shown that the size of the herded oil slick seems to influence the burning efficiency [1,6].

With the aim of providing further insights into the phenomena involved in the ISB with herding agents, and to address some of the above-described knowledge gaps, some small-scale experiments were carried out. This study was thus set up to investigate the ISB effectiveness of two chemically confined crude oils and their respective 25% water-in-oil artificial emulsions in small-scale, controlled laboratory experiments. Moreover, benchmark tests were carried out with physical confinement to establish comparisons. The crude oils were ANS (Alaska North Slope) and Grane, and two herding agents were used for this study, OP40 and ThickSlick6535 (TS6535). Several burning parameters related to ISB were therefore studied and were compared to physical confinement in the same scale. Some of these parameters were also compared to results from the literature. It should be noted that the current investigation is complimentary of two other studies: The herders' thickening effectiveness of two herders for ISB and the studies of environmental effects of the herding agents [23,24].

2. Experimental Method

2.1. Apparatus and experimental procedure

The experimental program consisted of several small-scale experiments in controlled laboratory conditions. A customized rig, the Crude Oil Flammability Apparatus (COFA), was used, see Figure 1. The COFA has previously been used to replicate realistic ISB scenarios in open waters, as the ratio of water to oil is high (1.95×10^3), which is also higher than in other experiments (20-100) [25]. The rig consists of a 1.0 m x 1.0 m x 0.5 m water basin with two sides made of stainless steel and the other two of heat-resistant glass. The rig was filled with 390 liters of distilled water. The water temperature was between 0 and 5 ˚C to mimic arctic / cold water conditions. 200 ml of fresh or artificially emulsified crude oil were used for all experiments.

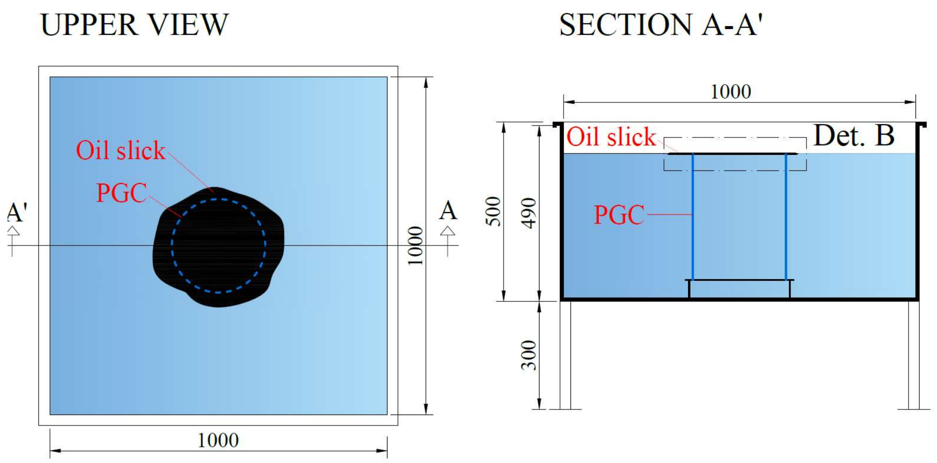


Figure 1 – Schematic of the experimental rig, PGC stands for Pyrex Glass Cylinder. The dimensions are in mm. Detail B is shown in Figure 2.

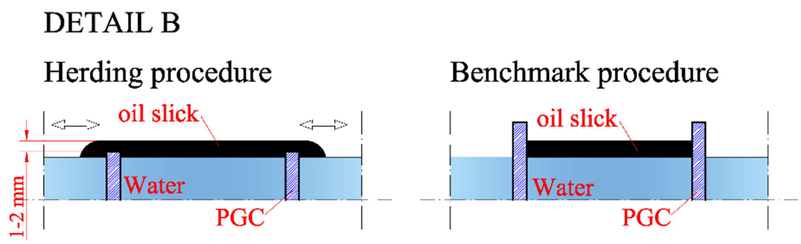


Figure 2 – Detail of the oil slick for the herding (left) and benchmark (right) experiments, PGC stands for Pyrex Glass cylinder.

Two sets of experiments were performed; one refers to the "herding experiments," where the crude oils were chemically confined and, and a second set of "benchmark experiments," where oil was physically confined. The latter served as benchmark testing for the study. Each of the herding experiments was made in triplicates to ensure the repeatability of the experimental procedure. In the case of the benchmark procedure, the experiments were performed once since previous experiments in the same rig showed good reproducibility (results with less than 10% variation) [4,25]. The exact procedure for each set of experiments is explained in the following.

- **The herding experiments:** After the basin was filled with cold water, a Pyrex glass cylinder was introduced in the center of the water bath; the surface water level was adjusted to be 10 mm from the upper edge of the cylinder. Thus, the cylinder did not interfere with the herding procedure. The required amount of fresh (0.2 L) or artificially emulsified crude oil (0.3 L) was carefully poured into the water bath and was let to expand for 30 minutes. Subsequently, 150 µl herding agent/m^2 of water surface, as operationally recommended [23], was applied drop-wise to the corners of the basin and was let to thicken the oil slick until it reached equilibrium. Then, the water surface level was slightly reduced by opening a valve in the bottom of the basin in order to obtain a 1-2 mm distance between the cylinder upper edge and the superficial water level, see Figure 2. During the herding, a camera placed above the basin was used to record the changing of the oil slick. The video recordings were analyzed using a binary MatLab code to estimate the oil slick thickness as a function of time. The herding thickening results are published elsewhere; the reader is referred to [26].
- **The benchmark experiments**: These experiments were designated as a benchmark to establish comparisons to the chemically-confined experiments, and these benchmark experiments represent fully confined conditions. When in-situ burning is performed in the field, fire-resistant booms are used, leading to fully confined conditions. In these experiments, this was mimicked by physically confining the oil slick within the hollow Pyrex glass cylinder, see Figure 2. All other parameters were as the "herding experiments".

The COFA's surfaces were exhaustively cleansed with a hot water solution of Alconox detergent (10 g/L) to discard possible herder residues. Additionally, surface water samples were taken to measure the surface tension in a Wilhelmy plate to confirm that no herder residues remained from previous experiments. If the water surface tension yielded values below 65 mN/m, the water was discarded, and the COFA cleaned once more before being refilled with water. Additionally, if any anomalies were observed during the expanding of the oil slick before herding, the experiment was stopped and re-done after further cleaning. Several samples of the fresh or emulsified oils were taken before and after each test to measure their physical properties such as the density and viscosities.

2.2. The experimental matrix

2.2.1. The variables in the experimental matrix: oil type, weathering degree and herder type

A matrix was designed taking into account three main variables, the oil type, the weathering degree and the herder type, respectively. Several parameters concerning the ISB of crude oil were then measured or estimated for each experimental condition. Crude oils are very different and can be classified according to the degree of, e.g. the density/viscosity, the evaporative losses, the content of resins, and the content of other compounds. For this study, two crude oils were selected, Grane and Alaska North Slope (ANS). The North Sea crude oil Grane is an asphalthenic crude oil with a high content of emulsion-stabilizing polar compounds like asphalthenes and resins. Therefore, it creates very stable emulsions [21]. In addition, Grane has a low content of light components resulting in a high density and low evaporative losses. ANS is a medium grade crude oil with a medium content of naphthenic components and a low content of paraffines. The artificial water-in-oil emulsions were made for both crudes by using a modified version of the rotatory flask technique and had a water content of 25 % [27]. The details of this technique can be found in [18]. It should be highlighted that this technique is not carried out according to ASTM F3045, which is a standard for preparing and classifying water-in-oil emulsions (that is not part of the current study's objectives)..

The physical properties of the fresh crude oils and their corresponding artificial water-in-oil emulsions are listed in Table 1. The values, for the density and viscosity, are averaged values measured in a Paar Stabinger Viscometer SVM 3000. The viscometer follows various standards for measuring kinetic viscosities (ASTM D7042, EN16896, and DIN 51659-2), the dynamic viscosity (ASTM D7042), and the density (EN ISO 12185, ASTM D4052, and IP 365).

Table 1 – Physical properties of the fresh and emulsified crude oils and the herding agents. The density and viscosity were measured by a viscometer, whereas the rest of the properties were extracted from the corresponding MSDS sheets.

Oil/ Herder	Density at 25 °C [g/cm^3]	Pour point [°C]	Viscosity at 25 °C [mPas]	Flash-point [°C]	SARA fractions hydrocarbon groups concentration [weight %][§]				
					Wax	Asphaltenes	Resins	Aromatics	Saturates
Grane	0.918	1.27	131.4	20-21	3.2	3	37	38	22
ANS	0.871	13.9	9.9	-4	2.6	4	6.1	15	75
Grane_25%	0.945		195.7	-					
ANS_25%	0.894		17.4	-					
OP40	0.989		10-40	>100*					
TS6535	0.830		7.6	57*					

*The properties of the herding agents were obtained from technical specifications and from Buist et al. [23].
[§]The SARA fractions were found in literature [28,29].

The artificial emulsions created for this study can be categorized as unstable emulsions following the definition of emulsion stability [17]. This is sufficient for this study as the 30 minutes of herding time is considered not to result in the breakup of the emulsions. In addition, unstable emulsions are preferred for this study as it was necessary to be able to ignite and burn the emulsions. A stable emulsion would most likely not have ignited.

Two herding surfactant agents were included in this study, OP40 and ThickSlick6535 (TS6535). OP40 is a silicone-based herder with high thermal stability and behaves like a liquid at room temperature. TS6535 is a mixture of Sorbitan Monolaurate and 2-ethyl-1butanol with 65 and 35% content, respectively. The herder properties are listed in Table 1.

2.2.2. The parameters

The "burning efficiency" or BE is a gravimetric estimation of the amount of oil consumed during the ISB method. The BE is obtained in percentage based on the initial oil amount, and it applies to experiments where oil and artificial emulsions were tested, and it can be calculated by the following equation:

$$BE\ [\%] = 100\ (1 - m_f/m_0) \qquad \text{Equation 1}$$

Here m_0 is the mass of the initial amount of crude oil, and m_f Is the mass of the oil residues left after burning. For artificial emulsions, only the initial oil amount was used, and the water was excluded from the BE estimations. During the ISB experiment with artificial emulsions, it was assumed that the water contained in the emulsion evaporates or mixes with the water in the tank.

Another relevant and directly applicable parameter or way to express the burning per unit time is the regression rate**,** which is the oil thickness deployment in time and is often expressed in mm/min and it is also based on gravimetric. The regression rate was estimated using the following equation:

$$\dot{r}''\ [mm/min] = 600\frac{\dot{m}_{global}}{A_s[(\rho_0+\rho_f)/2]} \qquad \text{Equation 2}$$

Here ρ_0 is the initial oil density expressed in g/cm³, ρ_f is the final oil density, and A_s is the oil slick area in cm².

The mass burning rate, $\dot{m}_{global}$, defines the mass lost per unit time of a substance (crude oil) burning and it is expressed in kg/s or g/s. Herein, the overall mass burning rate was studied, because it was not possible to measure the instantaneous weight loss during the experiments, as the entire assembly weighed too much. The global mass burning rate can be calculated by the following equation:

$$\dot{m}_{global}[g/s] = (m_o - m_f)/t_b \qquad \text{Equation 3}$$

Here t_b is the time duration of the burning experiment in seconds, m_0 is the mass of the initial amount of oil and m_f is the mass of the oil residues.

There is a large number of uncertainties in ISB and these are difficult to account for individually given the nature of the burning process [30]. All these previous gravimetric-based parameters are based on assumptions that carry uncertainties. This method assumes that the mass loss occurs through burning and it does not consider evaporation of the light components.

The evaporation effect was deemed negligible for the short duration of the experiments and given the relatively low evaporation rates of both oils [21]. Similarly, the dissolution of the oil components in water was not considered given the short duration of the experiment [7]. In addition, the water content in both oils was assumed to be minimal. Furthermore, the method assumes that all the post-burn residue was collected, which was carefully done after each experiment to minimize any residue being left in the oven. The post-burn residue was assumed to contain only heavy components, hence any evaporation of any left volatile components during the drying was deemed minimal.

Though the previous uncertainties were deemed to have only a small impact on the results, there were three uncertainties that had a more substantial influence on the measured parameters (burning efficiency, global mass burning rate and regression rate). First, the video camera's resolution resulted in 5% uncertainty for the slick area measurements [23]. Second, a random uncertainty was related to boilover, which was difficult to account for. In a specific set of experiment with water flows under the oil slick, the boilover was found to influence the results by 13%. Third, the thermal dissipation of the oil slick due to drifting and moving of the slick had a large impact on the results. Estimated uncertainties were especially large for the regressions rates (up to 50%). A detailed explanation of all the uncertainties can be found in

APPENDIX A.

3. Results and Discussions

3.1. Burning efficiency

The burning efficiency results obtained from all the experiments, herding and benchmark, are listed in Table 2. For the herding experiments, the data were averaged, and the corresponding standard deviation was calculated. The standard deviation was less than 8% in all cases, which confirmed the repeatability of the experiments. In the case of the benchmark experiments (without herder), only one experiment was performed for each test condition as stated in the previous Section.

The ISB experiments with fresh and emulsified ANS crude oils obtained greater burning efficiencies (BE) than those with Grane as seen in Table 2. The main difference between both crude oils lies in their physical properties. ANS is a medium grade crude oil with lighter compounds, whereas Grane has a large part of heavier components with a higher flashpoint and boiling point than ANS. To produce enough vapour gases for the combustion process, the temperature required to heat the fuel and counter the heat losses through the waterbed is higher for Grane than for ANS. Therefore, the BE obtained by Grane was expected to be lower.

On both fresh ANS and Grane crude oils, OP40 resulted in similar or slightly better BE than TS6335, as shown in Table 2. When comparing the emulsified crude oils, the opposite is observed, and TS6535 resulted in slightly higher BE than OP40. Based on these small-scale results, it is difficult to conclude which herder has a better impact on the burning behaviour.

In Table 2, a substantial difference in BE results is observed between the herding and benchmark experiments. The main difference between the experiments with and without herder was the transient heat transfer between the hot oil layer and the waterbed. In the benchmark experiments, the crude oil was physically confined whereas in the herding experiments the oil slick could to some extent move freely. As it was observed during the burning of the herded oil experiments, the oil slick also (re)expanded. In turn, the transient heat losses would increase due to an increased oil slick area (reduced slick thickness) affecting the heat balance, and it would dominate over the heat needed to vaporize enough fuel.

Moreover, the benchmark experiments obtained much larger burning efficiencies. In addition to the previous explanation, other phenomenon called "boilover" could potentially explain the BE differences as it was observed during the benchmark experiments for both crude oils (ANS and Grane). Boilover generated by the water boiling nucleation at the water/oil interface and splashing takes place when the water layer under the oil reaches a constant temperature close to the nucleation point of the water [31]. It leads to a violent burning of the fuel, an enlargement of the flame and a massive increase in the burning rate [32]. At the same time, boilover interrupts the burning process leading to extinguishment as it occurred in the control experiments.

For the herding experiments, including the benchmark tests, as seen in Table 2, the burning efficiency resulted in a substantial difference between the fresh and the emulsified crude oils. The emulsified crude oils obtained higher burning efficiencies than the fresh crude oils. This can in part be explained by the fact that, in contrast to the burning of pure oils on water, in-situ burning of emulsified oils involves different mechanisms where the main difference lies in the heat and mass transfer processes [1]. Comparisons with other relevant studies and in-depth analysis will be discussed in Section 3.1.2.

Table 2 – Summary of average burning efficiency results for both crude oils and their corresponding emulsions. Results from benchmark experiments (no herder) are also listed.

Test Type	Oil	Water content [%]	Oil (L)	Herder	Number of Repetitions	Slick Thickness τ_{oil} [mm]	Average BE ± SD [%]
Herding	ANS	0	0.2	OP40	4	4-6	37 ± 2.2
				TS6535	4	2-3	37 ± 3.3
		25	0.3	OP40	3	4-5	49 ± 6.2
				TS6535	3	4	55 ± 1.4
	Grane	0	0.2	OP40	3	5-6	26 ± 4.9
				TS6535	3	5	21 ± 3.3
		25	0.3	OP40	3	5-6	39 ± 2.9
				TS6535	3	3	48 ± 7.9
Benchmark	ANS	0	0.2		1	6	68
		25	0.3		1	6.5	67
	Grane	0	0.2		1	6	76
		25	0.3		1	7	78

3.1.1. Comparisons with other studies

A limited amount of experimental studies, ranging from small-scale to field experiments, using OP40 and TS6535 for ISB of ANS and Grane crude oils can be found in the literature [6–10,23,33]. The corresponding BE results along with the experimental details for each study are listed in Table 3. The similarities and differences in BE results between these studies and our results will be discussed in the following.

In a small rig (0.11 m²), experiments were conducted outdoor and with a 10% ice coverage, an averaged burning efficiency was obtained of 38% for 0.1 l. of fresh ANS herded with OP40 [8]. This low result is quite similar to the results obtained in our study with fresh ANS, see Table 3. There are many similarities in the experimental proceeding between the current study and the study reported by Bullock et al. [8]. The only difference is regarding the use of ice blocs (less than 10% coverage) in [8], which seems to have no substantial effect on the overall burning.

The burning efficiencies obtained by the herding experiments in this study are relatively low when compared to similar small-scale studies [6,23,33], see Table 3. The differences observed are due to the amount of oil used in our study was 0.2 l, which is lower compared to 0.4 l in [6,23,33]. Also, the contrast in the experimental set-up used for each study can also explain the differences in the burning efficiencies. An extractor close to the burning oil slick was extracting the smoke plume at 300 l/min was used in [6,23,33]. Such an extractor would have contributed to increasing the radial influx of oxidizer into the combustion zone. By contrast, in our case, the extraction system was placed at 1.3 m above the oil slick level, which minimized the influence of the mechanical extraction system. Another aspect of the rig in [6,23,33] is that the oil could move freely during combustion reaching the side walls made of steel. In turn, re-radiation from the walls would have potentially contributed to the combustion process [34].

The results obtained in large-scale and field experiments [7,9,10] resulted in much larger BE as compared to the results obtained in the current study, see Table 3. Despite the influence of other variables in those experimental studies, such as wind and waves, the higher BE can be attributed to the large amounts of crude oils employed in those investigations [7,9,10]. The heat and mass transfer mechanisms change as a function of the oil size [35]. Larger amounts of energy are generated as the size of the oil increases; in turn, larger BE can be expected.

The literature results might indicate whether the herder type can influence the overall burning process. Results from small-scale experiments reported by Buist and Meyer [33] showed that the experiment performed with OP40 attained a better BE as compared to the experiment with TS6535, see Table 3. In the large-scale study reported by Aggarwal et al. [7], the OP40 resulted in a slightly better BE for ANS than TS6535 for similar experimental conditions, see Table 3. Authors of both studies did not provide physical explanations for such a finding.

Table 3 – Burning efficiency results for other studies ranging from small- to large- scale size.

Rig size [m²]	Wind [m/s]	Waves	Ice coverage [%]	Evap. degree [%]	Temp [˚C]	Oil type	Herder	Oil vol. [L]	BE [%]	Ref.
0.11	NS	No	10	0	~1	ANS	OP40	0.1	38	[8]
10	0	No	0	0	~20	ANS	OP40	0.4	50	[33]
							TS6535	0.4	36	
10	NS	No	0	0	< 0	ANS	TS6535	0.2	49	[6]
								0.2	50	
								0.4	59	
			Yes (NS)					0.4	40	
10	No	No	0	0	NS	ANS	OP40	0.4	59	[23]
				10				0.4	46	
				27				0.4	56	
				0	NS		TS6535	0.4	49	
				0	NS	Grane	OP40	0.4	59	
							TS6535	0.4	40	
20	<1	No	0	0	~5	Grane	OP40	20	72	[9]
								20	78	
1800	< 3.3	No	10	NS	~ 10	ANS	OP40	70	86	[7]
								75	59	
								151	94	
							TS6535	155	73	
								155	86	
Field test	<4	No	0	5	NS	Grane	TS6535	3500	75	[10]
	<5							800	50	

NS = Not specified

The reviewed results from literature along with the current result indicate that the BE is dependent on the oil volume tested. In studies with oil volume larger than 0.4 L, the burning efficiency resulted in much higher burning efficiencies, which emphasizes the scalability of the phenomenon. The herder type seems to affect the BE somehow, which is in contrast to the results found in this study. It remains unclear how the herder type affects the burning behaviour during ISB as there are currently no physical explanations of the causes. The rest of the data from the literature indicates that as the oil slick size increases in volume and within the limits of achieving a minimum ignitable thickness, higher burning efficiencies will be achieved. Even though such behaviour in ISB is empirically known within the field, there is no such scaling analysis or theoretical correlation that could address the scalability trend.

3.1.2. The effect of weathering on BE

The BE results (behaviour) from various studies are summarised by the four trends shown in Figure 3. As seen, the burning behaviour of emulsions for in-situ burning is complex. It is difficult to elucidate which parameters affect the different trends and to which extent they influence the results. However, the peak in BE appears to be a phenomenon occurring in small-scale testing only.

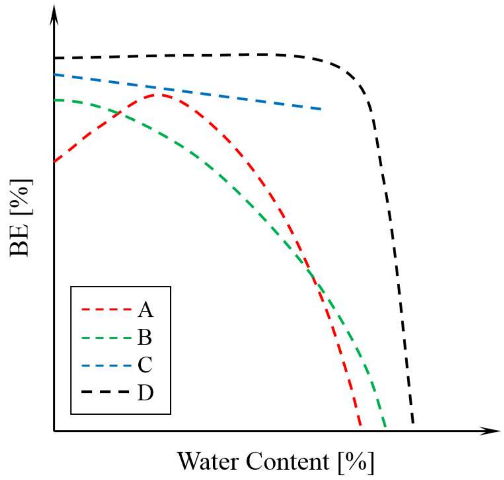


Figure 3 – Diagram of the burning efficiency behaviour based on the current investigation and various studies [21,36–40]. The current data and data from small-scale (Ø 0.1 to 1.1 m pool diameter) [21,36,38,39] fit curve A where the peak in BE is more pronounced for the smaller pools. Curve B is observed across various pool diameters (Ø 0.1 to 9.8 m) [21,36–38]. Other BE data (Ø 0.4 to 1.14 m) [37,40] does not decrease or decrease slightly (and linearly) as a function of the water content, and this behaviour is represented by curve C. Finally, curve D represents data from a meso-scale test in a 1.7 m diameter pool [21].

The boilover is hypothesized to be a phenomenon to occur in small-scale testing. A boilover-like behaviour was noticed throughout the burning and boilover occurred at the end of the experiments with artificial water-in-oil emulsions with both crude oils. When an emulsion burns, the top layer evaporates and provides a sufficient amount of flammable gases to sustain burning, whereas the emulsion layer takes up the heat for the oil layer and breaks up providing more oil to the hot layer [1,13]. The properties of the emulsion change with water content (boiling point and diffusivity) [41,42]. As a consequence, the heat losses to the water bed increases, which in turn leads to more intense boilover (the superheated water layer thickness). This hypothesis could explain the increase in BE as a function of the water content, see curve A in Figure 3. After a maximum in BE, the BE decreases as the water content increases further. This decrease might be due to the lower amount of oil in the emulsion having lower overall energy. Hence, the superheated water layer is not reached, and boilover intensity is reduced.

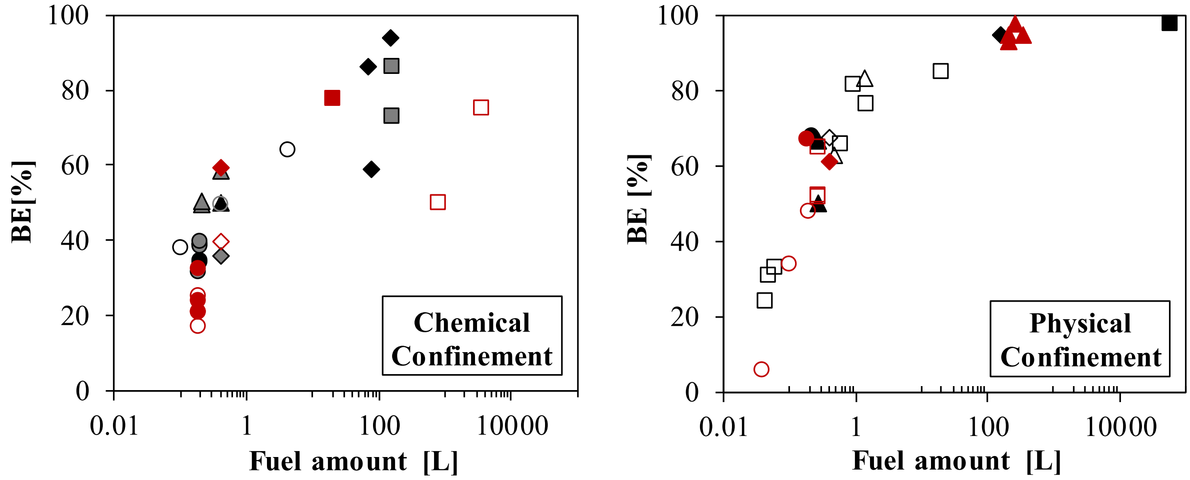
In the previous hypothesis, the emulsion is believed to fully (or almost) deplete where the heat losses and overall energy are determinant for boilover. In other cases (such as Curve B in Figure 3), the oil does not separate from the more stable emulsion at a sufficient pace to support burning (and counteract the heat losses). Consequently, extinction occurs and lower BE can be expected (lower than in non-weathered oils) as the water content increases. It is unknown and difficult to predict the mechanisms behind the other two curves (C & D) in Figure 3.

As seen, the BE behaviour of weathered crude oils shows that there are many parameters and uncertainties coupled with the problem. It is difficult to predict the mechanism behind these differences without an appropriate temperature measurement of the waterbed, the oil layer and the oil/emulsion layer to establish the heat balance. Vertical measurements have been performed in previous (fully confined) experiments with the same rig [4,43]. In the experiments with herder, horizontal measurements of the oil slick would also be necessary, as the drifting oil slick would complicate the measurements. The heat balance of emulsified crude oils is more complex since it would also depend on a range of parameters (the stability of the emulsion, the amount of water content in the emulsion, the size of the oil slick, convective and buoyant flows around the plume, radiative feedback from the flames and soot to the fuel surface, and liquid mass transfer mechanism in the liquid layer). Such discussions lie beyond the scope of the current investigation.

3.1.3. Scalability of the BE results

The BE results obtained in this study along with the results from the literature [6,8–10,23,33] are depicted in Figure 4 (left pane) as a function of the oil slick volume. It should be noted that the results from the literature were selected based on their experimental similarity with the current study. Results from various experimental studies along with field experiments involving ANS and Grane crude oils from [9,23,36,44–47], where the ISB experiments were performed with physical confinement, are also depicted in Figure 4 (right pane). Also, our results from the benchmark experiments are also illustrated in the same figure.

As seen in Figure 4 (left pane), there is a qualitative disparity between the results with chemical confinement or herding agents and the results with physical confinement. In the former, the BE is dependent on the oil amount for most of the results. The only exception is the data from [10]. The results presented in Figure 4 (left pane) show that for even similar oil amounts, the BE can vary primarily due to the substantial difference between testing methodologies found in literature, as it was earlier discussed. Despite these large variations, the overall BE data shows a linear dependency as a function of the oil amount. In contrast, the data that corresponds to ISB with physical confinement shows a distinctive behaviour, see Figure 4 (right pane).



Chemical Confinement				
Oil	Herder	Symb.	Comments	Ref.
ANS	OP40	●		Current
		▲		[33]
		◆	wind < 2 m/s	[7]
		○		[8]
	TS6535	●		Current
		◆		[33]
		▲		[6]
		■	wind < 3 m/s	[7]
		○		[23]
Grane	OP40	●		Current
		◆		[23]
		■		[9]
	TS6535	○		Current
		◇		[23]
		□	wind < 5 m/s	[10]

Physical Confinement				
Oil	Confinement	Symb.	Comments	Ref.
ANS	Ring	●		Current
		▲		[9]
		◆		[47]
	Boom	■	weathered oil	[46]
	Ice pool	□		[44]
	Ring	◇		[23]
		△		[36]
Grane	Cylinder	●		Current
		□		[9]
	Ring	◆		[23]
	Ice pool	▲	weathered oil	[21]
	Cylinder	○		[25]

Figure 4 – Comparison of the current burning efficiency results concerning results from similar studies. All the plotted data represents results with fresh or slightly weathered oils.

The BE data from physical confinement shows less dispersibility and an explicit dependency on the oil amount following two regimes. The first regime corresponds to small amounts of the oil slick (up to 2 l.) where the best fit would be an exponential curve. The second regime corresponds to large amounts of oil (> 100 l.), and the BE seems to be independent of the oil amount. The shift from the first regime to the second regime remains unclear as more data points would be required to define this zone. The physical explanation could potentially lie on the increasing radiative feedback to the combustion zone as the size of spilled oil increases [30]. Primarily, with the second regime, because it was found to become dominant in large size pools or a large amount of oil as the flame becomes turbulent [30].

The same cannot, however, be said for the ISB results with chemical confinement as seen in Figure 4 (left pane). For this case, the BE seems to be dependent within only the first regime that might not correspond to the case of physical confinement. In other herding experimental investigations with free-floating oil slicks, it has been addressed that the oil slick increased in area as the flame spread in all directions [23,48]. This behaviour is similar to what was observed in the current study. Such an expanding oil Slick during burning would have an important effect on the burning process. As a consequence, oil slicks chemically herded might result in lower BE as compared to physical confinement.

3.2. Global mass burning rate

The global mass burning rates for fresh and emulsified crude oil are shown in Figure 5. Fresh ANS has a general higher burning rate than what was seen for Grane. Differences in oil physical properties can potentially explain it as was discussed earlier. Emulsions generally have a higher mass burning rate than fresh oil regardless of the type of containment (chemical or mechanical). The mechanisms behind the ISB of emulsions might accelerate the burning process compared to the fresh crude oils. No clear trend is found regarding the two herders and their possible influence on the burning rate. Finally, the burning rate results from the benchmark experiments were substantially higher concerning the herding experiments. Again, the explanation lies in the heat losses to the waterbed being greater in the herding experiments since the oil slick expanded during burning.

The global mass burning rates for the fresh crude oils were used to estimate the regression rates and will be explained in Section 3.3.

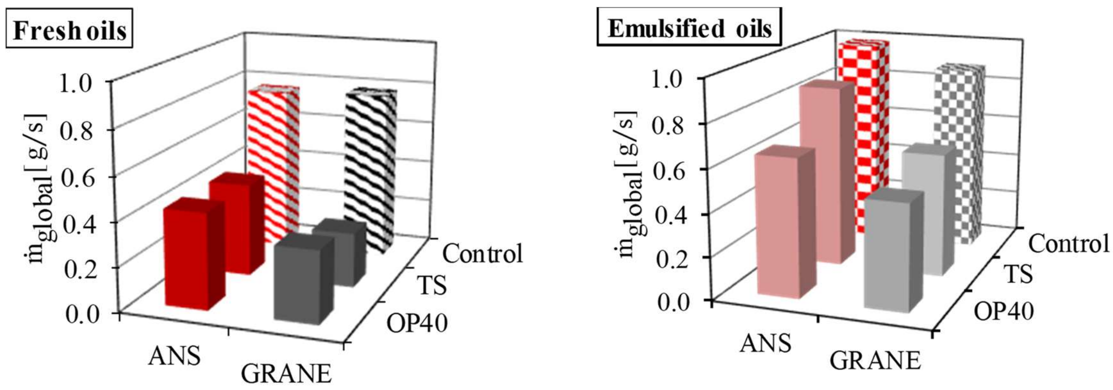


Figure 5 – Average global mass burning rate results for both crude oils and their corresponding artificial emulsion. Results from benchmark experiments (no herder) are also displayed.

3.3. Regression rate

Based on the global mass burning rates for the fresh crude oils (Section 3.2) and using Equation 2, the regression rates were estimated only for the fresh crude oils. The estimated regression rates in this study along with initial slick conditions (after herding) are listed in Table 4. Also, there are no dependencies for the regression rates as a function of the crude oil type. This finding is in contrast with previous results in Section 3.1 and Section 3.2 where the ANS resulted in higher values than Grane. It seems that the free movement of the herded oil slick during burning can have a large impact on the regression rates regardless of the oil type.

The initial slick conditions (thickness) seem to influence the estimated regression rate. As the herded oil slick increases in thickness (or reduces in slick areas), the regression rate increases. A thicker slick thickness would contribute to reducing the heat losses towards the underlying water bed, and thus higher regression rate would be expected. As in previous cases, the benchmark tests resulted in much higher regression rates than the herding experiments. The estimated regression rates will be compared against results from literature in the following section.

Table 4 – Summary of the regression rates results for both fresh crude oils.

Testing matrix			Slick thickness	Regression rate
Test type	Crude oil	Herder	τ_{oil} [mm]	$\dot{r}''$ [mm/min]
Herding	ANS	OP40	4.6	0.36
			5.7	0.51
			5.4	0.45
			4.9	0.37
		TS6535	3.8	0.16
			4.3	0.36
			4.3	0.33
			5.1	0.39
	Grane	OP40	5.6	0.50
			6.7	0.31
			6.3	0.36
		TS6535	5.8	0.36
			5.3	0.17
			5.4	0.23
Benchmark	ANS	None	6.2	0.95
	Grane		6.0	0.95

3.3.1. Comparison with other studies and scalability

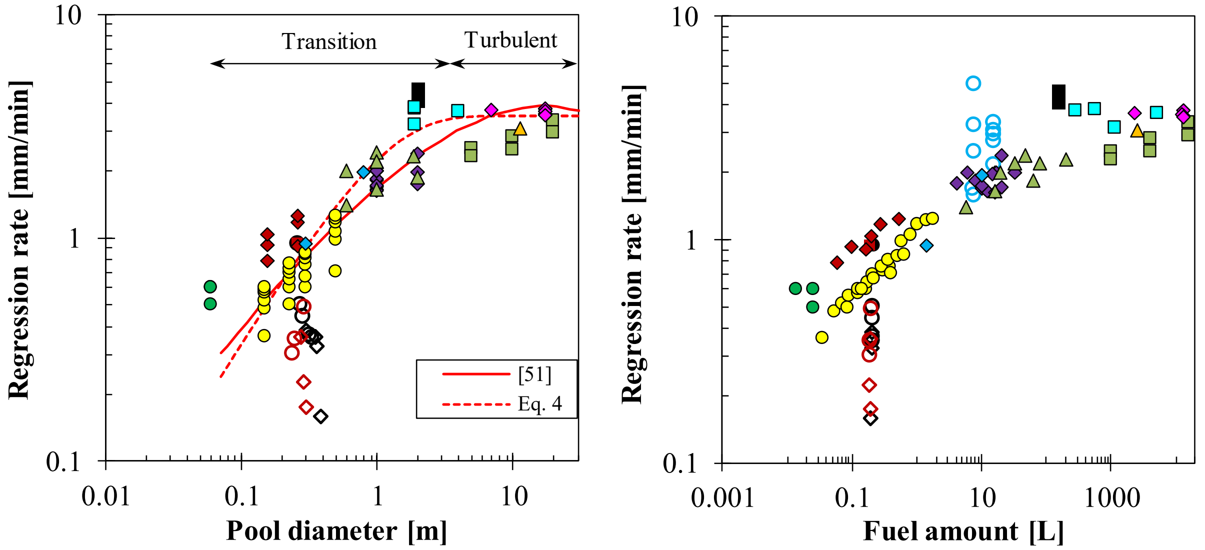
The regression rate from the herding and benchmark experiments are depicted in Figure 6 (left pane) along with regression data from other studies [31,41,47,49–55]. The corresponding experimental conditions from the literature are also gathered in the same figure. Koseki and Mulholland's correlating curve [51] is plotted in Figure 6 (left pane). Buist et al. [1] provided the following equation to correlate the regression rate of pool fires in the open.

$$\dot{r}'' = 3.5\,(1 - e^{-D}) \qquad \text{Equation 4}$$

Equation 4 is also depicted in Figure 6 (left pane).

As seen in Figure 6 (left pane, regression rate vs. pool diameter), for the different physical confined crude oils, it is clear that the results correlate in the same manner as the regimes (transition and turbulent) proposed by Blinov and Khudyakov [35]. The regression curve from Koseki and Mulholland [51] and Equation 4 predict qualitatively well the behaviour of the data from the literature. However, the data obtained from the small-scale herding experiments shows qualitative discrepancies as the regression rates lie lower than the results from mechanical confined oils. It is difficult to compare the herding data to mechanical data; most of the studies of ISB with herding agents do not report the regression rates as a function of the oil size in diameter.

The data from various studies scatters vertically, especially in the transition regime, see Figure 6 (left pane). It is clear that the parameter that contributes to the large dispensability of the data for each study is the initial oil slick thickness. This parameter affects the burning and combustion of crude oils. As the oil slick increases in thickness, the heat losses towards the water bed reduce since the oil slick acts as an insulating barrier. Thus the burning of the crude oil is enhanced [4]. However, the dispensability of the current herder results is due to the free movement of the herded slick during burning. As the herded oil slick expands during burning, the oil slick thickness is reduced. Consequently, the heat losses to the underlying waterbed might have been larger and resulted in lower regression rates.



Crude Oil	Confine-ment	Symb.	τ_{oil} [mm]	Comments	Ref.	Crude Oil	Confine-ment	Symb.	τ_{oil} [mm]	Comments	Ref.
ANS	OP40	○	3-4	COFA	Current	ASB*	Pool	◆	5-26		[49]
	TS6535	◇	1-3			Arabian light	Pan	□	50		[50]
Grane	OP40	○	4-5					△	NS		[56]
	TS6535	◇	3			K-A-O**	Pan	○	2-9		[31]
Kuparuk	TS6535	○	3-8	Ice < 30%	[6]	Louisiana	Pan	◆	54-61	Outdoors	[57]
ANS	Ring	●	4	COFA	Current	Murban	Pan	◆	20	Water bed	[41]
		■	50	Outdoors	[47]	Prudhoe	Ring	●	5-8		[53]
Grane	Cylinder	■	4	COFA	Current	Sarukawa	Pan	□	100-400	Outdoors	[54]
		◆	3-10		[25]	Statfjord	Pool	△	35	Evaporated	[55]

*ASB = Alberta Sweet Blend

**K-A-O = Kittiway (63%)-Arabian (33%)-Oural (4%)

Figure 6 – Regression rate as a function of the oil pool diameters (left pane) and as a function of the fuel amount (right pane).

The right pane in Figure 6 presents the same regression data as in the left pane (except the curves) but as a function of the oil volume. Additionally, regression data from a study where Kuparuk [6] crude oil was herded with TS6535 is included.

By presenting the regression rate as a function of the oil amount, two characteristic scales of pool fires (the pool diameter and the slick thickness) are included. The herding results along with the result from the literature show that the regression rate is a function of the oil amount, see Figure 6 (right pane). The same behaviour, seen previously in Figure 6 (left pane), can be observed in the regression rate data as a function of the oil amount (right pane).

The transition and turbulent regimes are also applicable to the regression rate data as a function of the oil amount for chemically and physically confined results. The shift from the transition to the turbulent regimes takes place between 10 and 100 L. These regimes correspond to the regimes identified previously for the BE results, see Section 3.1.2. It is not surprising to observe such behaviour, the oil volume inherently includes the pool diameter and initial oil slick thickness, and both are characteristic length scales of pool fires. There are no proposed correlations for the regression rate as a function of the oil amount, but it is an exponential curve, similar to Equation 4, would fit the data.

As seen in Figure 6 (right pane), the regression rates obtained with herded Kurapuk fits reasonably well the overall trend. However, the Kuparuk data scatters vertically, and some of the data over predict the general trend. Our data with herding agents slightly underpredicts the trend and also shows scattering. This behaviour observed in both, the current study and in [6], is also in line with the observation from other studies where the herder oil slick expanded as burning progressed, the same was observed in this study.

This finding suggests that there is also a scaling behaviour of ISB with herding agents similar to mechanically confined cases. Data from mechanically and chemically confinement proves that for the regression rate there a scaling relation from the small oil pool/amount to larger sizes but with contrasting qualitative differences between both methods. Therefore, it is required to further study the burning behaviour of chemically confined crude oils for ISB.

3. Conclusion and further work

Several small-scale experiments in laboratory conditions were conducted to study the effect of two herding agents (OP40 and ThickSlick6535) on the ISB over two fresh crude oils, ANS and Grane, and their corresponding artificial emulsions. It should be noted that the ISB behavior observed during the small-scale experiment should not be directly extrapolated to real large-scale scenarios. Instead, the results should be taken as illustrative and would encourage future research. The main findings are presented in the following.

The burning behaviour during ISB (BE and $\dot{m}_{global}$) showed dependencies according to the oil type due to the difference in oil properties for each oil. The exception was in the regression rates ($\dot{r}''$) results where the free movement of the herded oil slick during burning had a large impact.

At this small-scale, no explicit dependencies of the herder type on the ISB behaviour (BE, $\dot{m}_{global}$ and $\dot{r}''$) were observed. Perhaps at large scales, such a dependency would arise as a few results from the literature indicate that OP40 results in higher BE than TS6535.

The weathering degree of the crude oil results in qualitative differences in burning behaviour (BE and $\dot{m}_{global}$). The heat and mass transfer mechanisms of emulsified oils are different from fresh crude oils.

Quantitatively lower results (BE and $\dot{m}_{global}$) are obtained by using herders when compared to physical confinement. Chemical confinement allows the oil to spread during burning that can explain the lower results as compared to physical confinement.

The BE results were lower compared to most of the previous similar studies due to differences in experimental conditions and oil size. Scalability of both the BE and $\dot{r}''$ was observed as a function of the oil amount (in volume and pool diameter). However, the scalability dependencies were qualitatively different between chemical and physical confinement.

The ISB behaviour observed in the current study along with comparisons to other studies shows quantitative and qualitative discrepancies of herded oils slick as compared to physical confinement. The influence of the free moving herded oil slick on the ISB merits further study and the scalability of the phenomenon as well.

Acknowledgment

This paper was prepared under contract for the International Association of Oil & Gas Producers (IOGP) by S.L. Ross Environmental Research Ltd as the prime contractor. Publication of this paper does not necessarily imply that the contents reflect the views and policies of IOGP, nor are there any implied IOGP endorsements of studies performed and results presented by SL Ross or by the subcontracting partners DCE and DTU. The authors would like to thank Bjørn Skjønning Andersen for his assistance during the experimental part of the work.

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APPENDIX A

A. Uncertainty in a single measurement
    a. Resolution: the effect of these uncertainties can be deemed negligible, except for the last one (slick area measurements).
        i. Weight measurements: The precision balance MS4002TSDR/00 has a precision of 0.01 g.
        ii. Density measurement: The PAAR viscometer 400 SV had a precision of 0.0002 g/cm^3.
        iii. Time measurement: the video camera had a precision of 0.033s.
        iv. Slick area measurement: the video camera had a precisions of 0.01px. However, due to distortion the final error is lower than 5% [23].
    b. Calibration: The scale and the viscometer were calibrated on a monthly basis.

B. Uncertainties in the mean:
    a. Systematic
        i. Offset and gain: Since all the instruments were calibrated following the manufacturer's specifications, no offset nor gain uncertainties were observed in the results.
    b. Random: the last two categories in the random uncertainties had a large impact on the results variability.
        i. Mass losses through evaporation: The gravimetric method assumes mass loss trough burning. Both oils evaporate (ANS at 3-4% and Grane less than 1% after one hour). However, given the short time between releasing the oil and burning it (< 1 h), these can be deemed negligible [7].
        ii. Dissolution of soluble components: The dissolution of the oil components in water is not contemplated, given the short time, it can be considered negligible [7].
        iii. Water content in the oil: For ANS the water content is < 0.1%, and for Grane there is no data available but oils from near platforms also have very low water content.
        iv. All residues collected and weighted: Small amounts of the residue might have dropped in the oven (where samples were dried out), this can be considered a very small amount compared to the total amount of oil.
        v. Post-residue evaporation in the oven: Most of the volatile components in the oil were assumed to evaporate during burning, as was demonstrated by van Gelderen and co-workers [43].
        vi. Weathering degree: Density measurements were repeated three times in the Viscometer to make sure the artificially weathered crude oils were similar. But small discrepancies were noticed (for the density, the largest uncertainty in the mean was 0.0004 g/cm3 and 0.0005-0.0019 the standard deviation).
        vii. Boilover: Boilover is a common phenomenon in laboratory conditions and in industrial storage applications. In in-situ burning in open water, boilover has not been reported so far. One would think that the thermal dissipation in the ocean is much greater (due to the infinite water column and seawater currents) that nucleation of the water layer under the oil may never reach nucleation. We conducted alternative experiments in the rig with physical confinement (in a 16 cm diameter cylinder) but with a water pump that created a water flow, the BE results were lower than in experiment with still water, see Figure A.1. It is clear that adding a water flow under the oil layer

can reduce the BE in a 13%. Hence, boilover is one of the parameters that creates a large variability in results across literature (in small-scale tests). Reducing the boilover will lead to creating similar conditions as those in real scenarios.

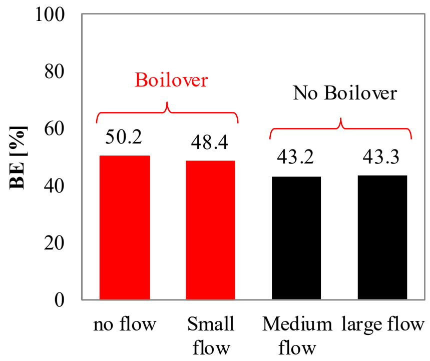

Figure A. 1– BE results with fresh Grane oil as a function of the pump flow.

viii. Thermal dissipation: In the herding experiments, the oil slick expanded and contracted during burning, as a consequence the thermal dissipations from the hot oil layer to the water bed varied largely from test to test. The variability was especially significant in the regression rate results. Unfortunately, this had a large impact on the results and could not be controlled as it can be seen in Table A. 1. The uncertainty (in percentage) was considerable in the BE results, but it was particularly substantial in the regression rates.

Table A. 1 – Estimated uncertainties (in percentage) for the burning efficiency and regression rate values.

Oil	Water content [%]	Oil (L)	Herder	Number of Repetitions	Average BE [%]	Percentage uncertainty in BE [%]	Regression rate $\dot{r}''$ [mm/min]	Percentage uncertainty in $\dot{r}''$ [%]
ANS	0	0.2	OP40	4	37	12 to 22	0.42	12 to 17
			TS6535	4	37	-2 to 19	0.31	23 to 56
	25	0.3	OP40	3	49	6 to 26	-	-
			TS6535	3	55	28 to32	-	-
Grane	0	0.2	OP40	3	26	-24 to 20	0.39	16 to 26
			TS6535	3	21	-12 to 24	0.25	22 to 47
	25	0.3	OP40	3	39	16 to 29	-	-
			TS6535	3	48	-17 to 22	-	-